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THE ADSORPTION OF IRON DURING ETCHING OF LITHIUM FLUORIDE CRYSTALS

by

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The action of cation inhibitors in aqueous solutions on the etch morphology of cleavage surfaces of lithium fluoride has been exhaustively studied by Gilman, Johnston and Sears [1]. Of some thirty cations investigated only two, iron and aluminum produced etchants that would form regular square dislocation etch pits. Gilman et al. concluded that the inhibitor ions, which need only be presented in concentrations of the order of one part in 10^6 must be (a) within 25% of the size of the Li^+ion, (b) have a stable fluoride salt with low solubility and (c) form a stable fluoride complex. These criteria suggest that such ions will adsorb readily at cation sites on the crystal surfaces, and thereby modify the dissolution conditions. That so few ions are necessary in solution to profoundly modify the etch morphologies suggests that they adsorb preferentially at the primary dissolution sources, viz kinks in crystal ledges [1,2].

The present experiments were undertaken to investigate this possibility by relating the spatial distribution of adsorbed ferric ions to the etch morphologies. Etching of freshly cleaved $\{100\}$ surfaces of lithium fluoride was carried out in dilute aqueous solutions of ferric chloride containing radioisotope Fe^{59} of known activity. After washing, the etched surfaces were placed on nuclear photographic emulsion and the distribution of radioactivity deduced by track-autoradiography. Preliminary experiments established that the washing procedures after etching produced a reproductible activity independent of washing time.

An early observation demonstrated that there is no (detectable) dependence of ferric ion adsorption on dislocation etch pit density, manifest as a constant track density over the whole of a given crystal surface. (Exceptions include large adsorption at gross defects, such as high cleavage steps, etc.) Any variations in track density with location of surface area measured are included in the statistical deviations of the mean results of track-counting fifteen areas per surface.

Using a ferric chloride stock solution of known specific activity of iron, a series of etchants was prepared of varying iron content and two lithium fluoride samples etched for two minutes in each. There is no observable change in adsorption for etching time greater than 3 seconds. The ferric ion adsorption, measured as track densities (corrected for background) and converted to ions/cm^2, is represented by the adsorption isotherm of Fig. 1. The isotherm is seen to exhibit a definite inflection corresponding to a mean iron coverage of about 3.5×10^{13} ions/cm^2, and occuring in the range of iron concentration in the bulk solution of from 0.2 to 2.0×10^{-6} parts by weight.

Observation of dislocation etch pit morphology as a function of iron concentration followed the form first pointed out by Gilman et al [1] and is demonstrated by the interference micrographs of Fig. 2. Correlation with the isotherm shows that the optimum etchant concentration (to produce square-based dislocation etch pits)

corresponds closely to the point of inflection of the adsorption. At larger ferric ion concentrations, when adsorption increases, rounded pits are observed. At lower concentrations, terraced shallow pits correspond to less iron adsorption These results are consistent with recent theoretical ideas on the effect of inhibitor on kink motion [2].

It should be realised that the whole surface of an ionic crystal is not available to an adsorbing cation [3]. Assuming such an adsorbate to be formed as a monolayer when all cation surface sites are filled, it is found that for {100} surfaces of lithium fluoride, monolayer adsorption exists at 1.23×10^{15} ions/cm^2. On this scale, the adsorption inflection of Fig. 1 occurs at 1/35 of a monolayer of ferric ions.

Employing the established concepts of adsorption theory, this inflection may correspond to the complete filling of a particularly favourable type of adsorption site on a heterogeneous surface. It is attractive to suppose that these more favourable sites for the ferric ions are the kink-sites proposed by Gilman et al [1]. The inflection then corresponds to "monokink" adsorption. This suggests that in the range of optimum etchant concentration of iron, there will be, on the average, only three kinks in every hundred possible surface sites, the remainder comprising close-packed surface and straight ledges. This low density of kinks will cause the crystal

surface to appear macroscopically composed of only ledge-surface $\{0kl\}$[2]. This is observed in the form of flat-faced $\{0kl\}$ pyramidal etch pits at points of dislocation emergence. Furthermore, for a uniform coverage of 1/35 of a monolayer, the absorbed ions will be about six sites apart in a square array and this is approximately the spacing between monomolecular ledges on etch pit sides. This correlation suggests that dissolution morphologies are subject to part-poison, part-diffusion control[4] wherein the latter exists by the interaction of hemispherical diffusion fields centered on the dissolving kink-sites. The hemispheres can then interact both between kinks in the same ledge and between kinks in adjacent ledges. Also, since uniform iron coverage is observed, it is proposed that the whole crystal surface is composed, during dissolution, of $\{0kl\}$ facets inclined to the close packed $\{100\}$ plane at the same angle as the faces of etch pits. These other "surface" facets are not resolvable, however, since they are never able to attain sufficient size, due to the lack of a constant dissolution source. In many instances there is a suggestion of a surface mottle which could represent such facets.

Application of the Gibbs adsorption isotherm equation[5] to the results of this investigation allows for an estimate of the mean kink free energy, as follows. One form of Gibbs equation may be written as

$$\frac{d\gamma}{d(\ell_{nc})} = -\Gamma kT$$

relating the rate of change of surface free energy γ with the natural logarithm of the bulk concentration of adsorbate, c, to the surface excess Γ. Thus a curve of surface energy plotted against ($\ell n_e c$), will have instantaneous slope $-\Gamma kT$. Since we know Γ as a function of c, from the isotherm, we can therefore construct such a curve. This was done geometrically and the result is reproduced in Fig. 3. Arbritarily taking a bulk concentration of 2×10^{-6} for monokink adsorption, we obtain a measure of $\Delta\gamma$, the change in surface free energy due to the adsorption, as 6.1 erg/cm^2. Although the surface energy of a kink is not reduced completely to zero when it is filled with adsorbate, it can be assumed that a large fraction of its energy is reduced in this process and the value obtained can be taken as a lower limit to the energy of a kink-site in a lithium fluoride surface. These results give such a kink energy as 1.56×10^{-13} erg/kink, which appears to be of the correct order of magnitude, since it predicts a surface energy of a high index surface (maximum kink density) of approximately 200 ergs/cm^2 This compares favourably with the value of interfacial free energy of a {100} lithium fluoride surface in water of $\gamma_{LiF\text{-}H_2O}$ = 177 erg/cm^2, used in a previous study [4].

In order to further delineate the kinetics of inhibitor adsorption in this system, it is necessary to deduce isotherms at other temperatures and under-saturations, and this work is in preparation.

A complicating feature of the system is its dynamic nature, in that the surface is continuously dissolving at a rate which, on the atomic scale, is considerable.

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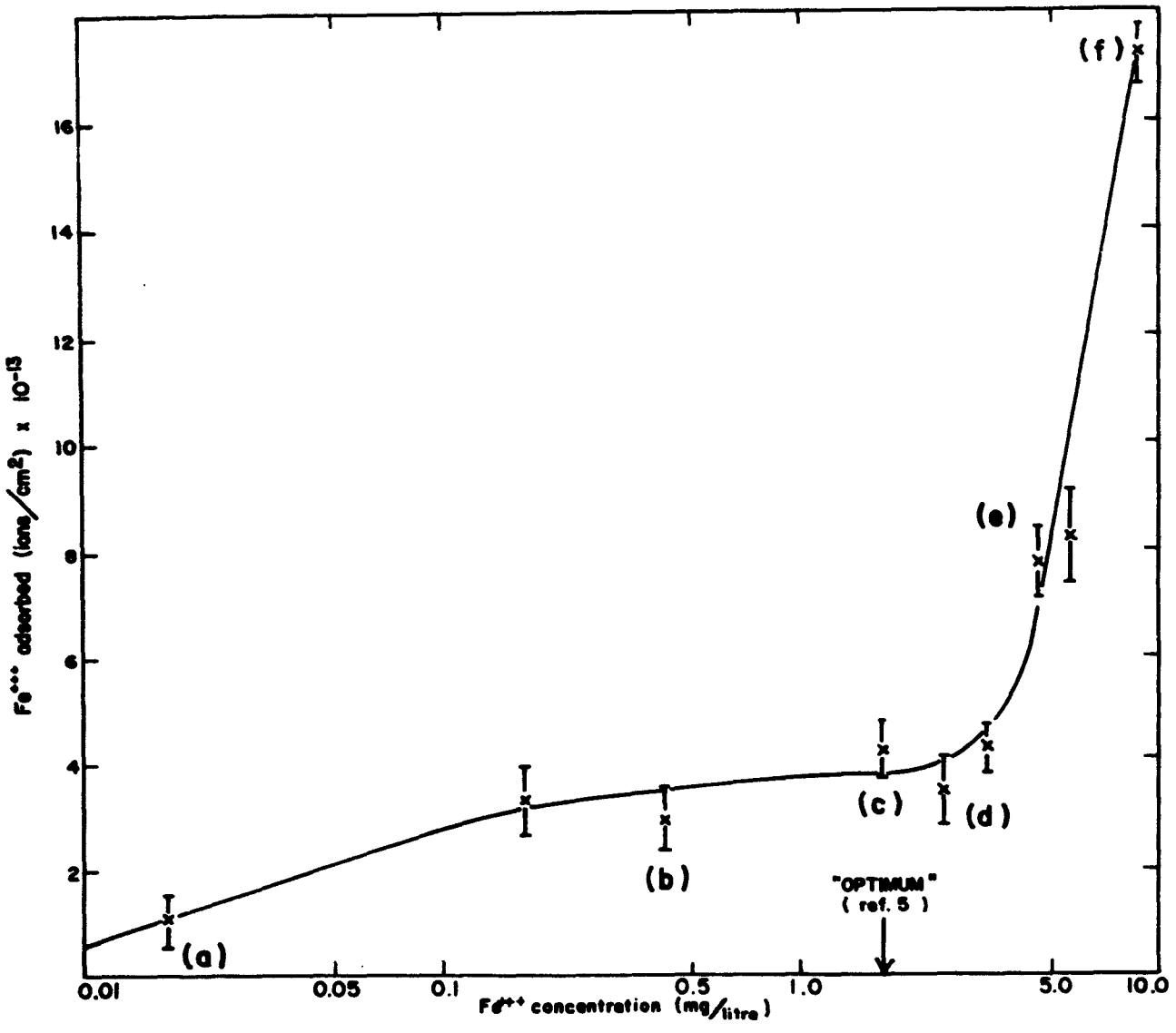
5. See, for example, S.Brunauer, "The Adsorption of Gases and Vapors", Vol. 1, (Princeton University Press, Princeton 1945).

CAPTIONS TO FIGURES

Fig. 1. Adsorption isotherm for ferric ions on a {100} cleavage surface of lithium fluoride at 22°C. (The figures (a) (b), (c), etc. refer to the bulk iron concentrations at which the micrographs of Figure 2 correspond).

Fig. 2. Interference micrographs of dislocation etch pits on lithium fluoride surfaces etched in aqueous solutions of ferric chloride containing (a) 0.017, (b) 0.42, (c) 1.7, (d) 2 5, (e) 4.6, (f) 8.4 mg Fe^{+++}/litre.

Fig. 3. Surface free energy of lithium fluoride surface as a function of the natural logarithm of the bulk solution concentration of ferric ions. Constructed geometrically.


(f)
16
14
12
10
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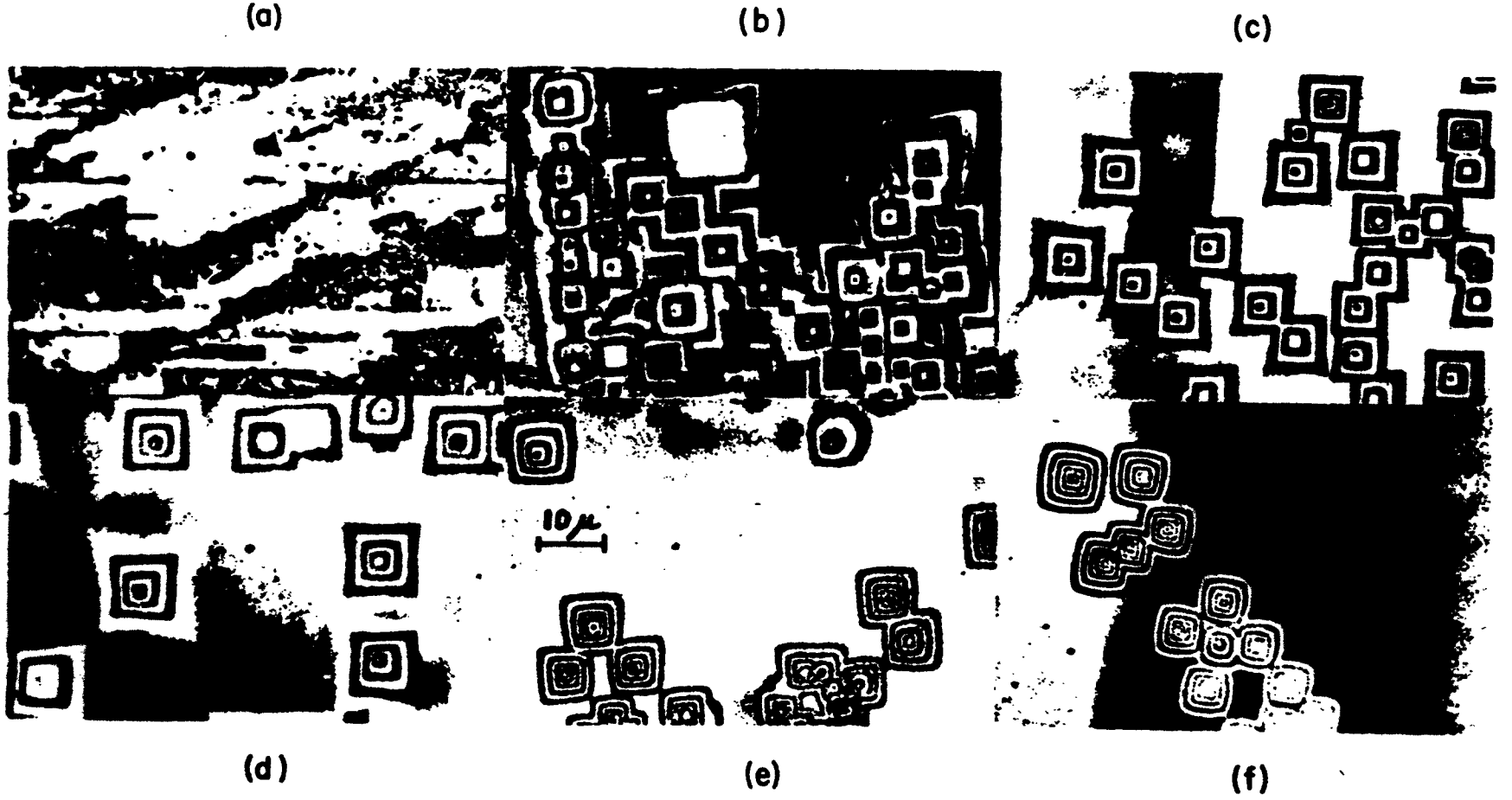
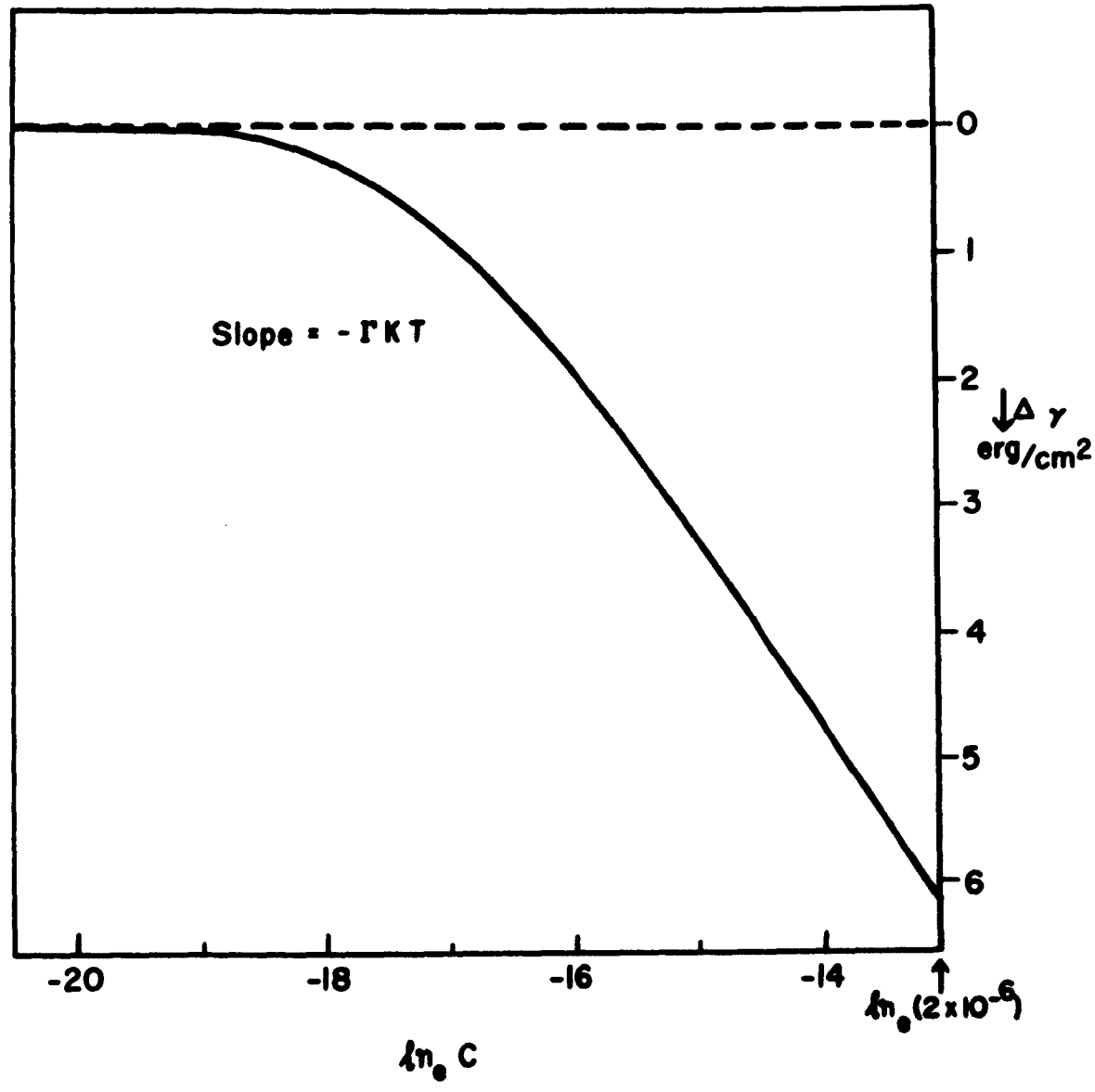
6
4
2
(e)
(c)
(d)
(b)
(a)
"OPTIMUM"
(ref. 5)
0.01
0.05
0.1
0.5
1.0
5.0
10.0
Fe++ concentration (mg/litre)
Fe++ adsorbed (ions/cm2) x 10-13


(a)
(b)
(c)
10μ
(d)
(e)
(f)


Slope = - Γ K T
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1
2
3
4
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↓Δ γ
erg/cm²
-20
-18
-16
-14
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ln_a (2x10⁻⁶)
ln_a C